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Determination of Dithiocarbamate Pesticides in Wastewaters

Battelle Columbus Labs., OH

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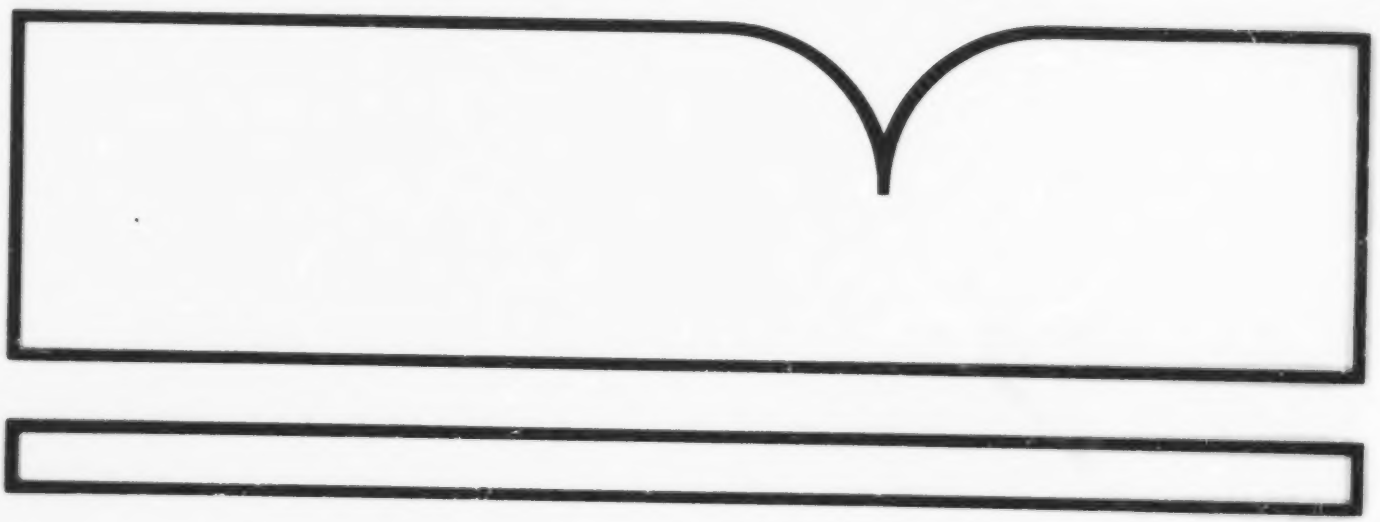

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DETERMINATION OF DITHIOCARBAMATE PESTICIDES IN WASTEWATERS

by

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The final method was applied to a wastewater obtained from a manufacturer of a dithiocarbamate in order to determine the precision and accuracy of the method. The wastewater contained high levels of dithiocarbamate and was diluted 1000:1 with Columbus POTW secondary effluent prior to its use in validation studies. The diluted wastewater was spiked with the 13 individual dithiocarbamate pesticides at the 50 and 100 µg/L concentration levels. Recoveries were greater than 82 percent for all of the dithiocarbamates except for EXD, nabam and nabonate. EXD and nabonate are not structurally true dithiocarbamates, which might cause consistently low recoveries. The quality of the standard used for nabam recovery studies was in question. Method detection limits (MDLs) in wastewaters may be higher due to interfering compounds.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory-Cincinnati conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.

- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.

- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This report is one of a series that investigates the analytical behavior of selected pesticides and provides a validated test procedure for their measurement in wastewater.

Robert L. Booth, Director
Environmental Monitoring and Support
Laboratory-Cincinnati

ABSTRACT

A method was modified and validated for the determination of dithiocarbamate pesticides in wastewaters. The developed method consists of sample pH adjustment to pH 12.2; removal of indigenous CS_2 by purging in a vortex evaporator; acidification of the sample to hydrolyze dithiocarbamate pesticides to form CS_2; extraction of the CS_2 from the sample into hexane; and determination of the CS_2 by gas chromatography using a Hall detector in the sulfur mode.

The final method was applied to a wastewater obtained from a manufacturer of a dithiocarbamate in order to determine the precision and accuracy of the method. The wastewater contained high levels of dithiocarbamate and was diluted 1000:1 with Columbus POTW secondary effluent prior to its use in validation studies. The diluted wastewater was spiked with the 13 individual dithiocarbamate pesticides at the 50 and 100 µg/L concentration levels. Recoveries were greater than 82 percent for all of the dithiocarbamates except for EXD, nabam and nabonate. EXD and nabonate are not structurally true dithiocarbamates, which might cause consistently low recoveries. The quality of the standard used for nabam recovery studies was in question. Method detection limits (MDLs) in wastewaters may be higher due to interfering compounds.

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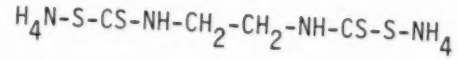
SECTION 1

INTRODUCTION

The research covered in this report is a continuation of the research under EPA contract 68-03-2956. The group of compounds originally designated as dithiocarbamates for method development and validation purposes is comprised of 19 compounds: amobam, AOP, Busan 40, Busan 85, EXD, ferbam, KN-methyl, mancozeb, maneb, metham, nabam, nabonate, Niacide, polyram, sodium dimethyldithiocarbamate (NaDMDTC), thiram, ZAC, zineb, and ziram. The method is based on the determination of carbon disulfide (CS_2) which is evolved from the dithiocarbamate moiety upon acid hydrolysis. The method is not specific for any of the dithiocarbamates, but is applicable to all of them.

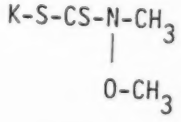
Amobam (I) is used to react with zinc sulfate to form zineb as a tank-mix fungicide spray.



I

The CAS registry number of amobam is 3566-10-7 and the IUPAC name for amobam is diammonium ethylenebisdithiocarbamate. Common synonyms for amobam include "Dithane Stainless" and "Chem-o-bam". Amobam has an acute oral LD_{50} in rats of 395 mg/kg.

Busan 40 (II) is used as a fungicide.



II

The CAS registry number for Busan 40 is 51026-28-9. Busan 40 is sometimes referred to as "Bunema".

Busan 85 (III) is used as a fungicide.

$$K\text{-}S\text{-}CS\text{-}N\text{-}(CH_3)_2$$

III

The CAS registry number for Busan 85 is 120-03-0 and the IUPAC name for Busan 85 is potassium dimethyldithiocarbamate.

EXD (IV) is used as a herbicide.

$$C_2H_5\text{-}O\text{-}CS\text{-}S\text{-}S\text{-}CS\text{-}O\text{-}C_2H_5$$

IV

The CAS registry number for EXD is 502-55-6 and the IUPAC name for EXD is O,O-diethyl dithiobis(thioformate). Common synonyms for EXD include "Herbisan" and "Sulfasan". Although EXD is not a dithiocarbamate, the potential exists in its structure for the formation of CS_2 upon treatment with acid. For this reason, it was included in this method.

Ferbam (V) is used for the protection of foliage against fungal pathogens.

$$[(CH_3)_2\text{-}N\text{-}CS\text{-}S\text{-}]_3Fe$$

V

The CAS registry number for ferbam is 14484-64-1 and the IUPAC name for ferbam is iron tris(dimethyldithiocarbamate). Ferbam has an acute oral LD_{50} in rats of >4000 mg/kg. Common synonyms for ferbam include "Ferbnate", "Hexaferb", "Karbam Black", "Aafertis", "Fuklazin", "Liromate", "Bercema Ferta 50", "Fuklasin Ultra", "Ferberk", and "Fenadow".

KN-Methyl (VI) is a soil fumigant.

$$K\text{-}S\text{-}CS\text{-}NH\text{-}CH_3$$

VI

The CAS registry number for KN-Methyl is 137-41-7 and the CAS name for KN-Methyl is methyl carbamodithioic acid potassium salt. A synonym for KN-Methyl is "PNMDC".

Mancozeb (VII) is a protective fungicide.

$$[\text{-S-CS-NH-CH}_2\text{-CH}_2\text{-NH-CS-S-Mn-}]_x(\text{Zn})_y$$

VII

The CAS registry number for mancozeb is 8018-01-7 and the CAS name for mancozeb is [[1,2-ethanediylbis[carbamodithiato]](2-)]manganese mixture with [[1,2-ethanediylbis[carbamodithioato]](2-)]zinc. Common synonyms for mancozeb include "Manzeb", "Maneb-zinc", and "Dithane M-45". Mancozeb has an acute oral LD_{50} in rats of >8000 mg/kg. Mancozeb is insoluble in water and organic solvents.

Maneb (VIII) is a protective fungicide effective against many diseases of foilage.

$$[\text{-S-CS-NH-CH}_2\text{-CH}_2\text{-NH-CS-S-Mn-}]_x$$

VIII

The CAS registry number for maneb is 12427-38-2 and the IUPAC name for maneb is polymeric manganese ethylenebis(dithiocarbamate). Common synonyms for maneb include "Manzate" and "Dithane M-22". The acute LD_{50} for maneb for rats is 6750 mg/kg. Maneb is insoluble in water and organic solvents. Maneb is stable under normal storage conditions, but decomposes on exposure to moisture with the formation of etem.

Metham (IX) is a soil fungicide, nematicide and herbicide with a fumigant action.

$$\text{CH}_3\text{-NH-CS-S-Na}$$

IX

Its activity is due to decomposition to methyl isothiocyanate. The CAS registry number for metham is 137-42-8 and the CAS nomenclature for metham is methylcarbamodithioic acid. Common synonyms for metham include "Metham-sodium", "Vapam", "VPM", and "Sistan". Metham has an acute oral LD_{50} for rats of 820 mg/kg. Metham is an irritant to the eyes, skin, and mucous membranes.

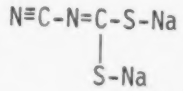
Nabam (X) has been used as a protective fungicide although it has been found too phytotoxic for general use on foliage.

$$\text{Na-S-CS-NH-CH}_2\text{-CH}_2\text{-NH-CS-S-Na}$$

X

The CAS registry number for nabam is 142-59-6 and the IUPAC name for nabam is disodium ethylenebis(dithiocarbamate). Common synonyms for nabam include "Parzate", and "Dithane D-14". Nabam has an acute oral LD_{50} of 400 mg/kg.

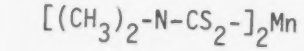
Nabonate (XI) is used as a fungicide.



XI

The CAS registry number for nabonate is 138-93-2 and the CAS nomenclature for nabonate is cyanothioimidocarbonic acid. A synonym for nabonate is "DCDIC".

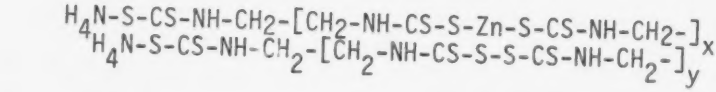
Niacide is a fungicide sprayed on apple and pear foliage. It is a mixture of manganous dimethyldithiocarbamate (XII) and mercaptobenzothiazole.



XII

Niacide has an acute oral LD_{50} for rats of 1500 mg/kg. Only one manufacturer of Niacide was identified and this manufacturer had not produced Niacide for over five years. No sources of standards for this pesticide were identified. Niacide was not included in this study.

Polyram (XIII) is a nonsystemic fungicide used for foliage application.



XIII

The CAS registry number for polyram is 9006-42-2 and it is a mixed precipitation product consisting of the ammonia complex of zinc ethylenebis(dithiocarbamate) and polyethylenebis(thiuram disulfide). Polyram is commonly referred to as "metiram". Polyram has an acute oral LD_{50} in rats of >10,000 mg/kg. Polyram is not soluble in water or organic solvents.

Sodium dimethyldithiocarbamate (NaDMDTC) (XIV) is a fungicide.

$$Na\text{-}S\text{-}CS\text{-}N\text{-}(CH_3)_2$$

XIV

The CAS registry number for NaDMDTC is 128-04-1.

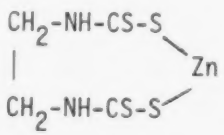
Thiram (XV) is a protective fungicide suitable for application to foliage or fruit.

$$(CH_3)_2\text{-}N\text{-}CS\text{-}S\text{-}S\text{-}CS\text{-}N\text{-}(CH_3)_2$$

XV

The CAS registry number for thiram is 137-26-8 and the IUPAC name for thiram is tetramethylthiuram disulfide. Common synonyms for thiram include "Arasan", "Tersan", "Ponarsol", "Ferna-Col", and "Fernasan". Thiram has an acute oral LD_{50} in rats of 80 mg/kg.

Zineb (XVI) is a fungicide used to protect the foliage and fruit of a wide range of crops.



XVI

The CAS registry number for zineb is 12122-67-7 and the IUPAC name for zineb is zinc ethylenebis(dithiocarbamate). Common synonyms for zineb include "ENT 14 874", "Dithane Z-78", and "Parzate". Zineb has an acute oral LD_{50} in rats of >5200 mg/kg.

Ziram (XVII) is a protective fungicide used on fruit and vegetable crops.

$$[(CH_3)_2\text{-}N\text{-}CS\text{-}S\text{-}]_2Zn$$

XVII

The CAS registry number for ziram is 137-30-4 and the IUPAC name for ziram is zinc dimethyldithiocarbamate. Common synonyms for ziram include "Milbam", "Zerlate", "Fuklasin", and "Aaprotect". Ziram has an acute oral LD_{50} for rats of 1400 mg/kg.

In general, dithiocarbamates are moderately stable in water under very basic conditions. A CS_2 generation method followed by determination of the CS_2 by GC-Hall analysis was the selected approach. The CS_2 is generated from the dithiocarbamate upon treatment with a stannous chloride ($SnCl_2$)/ hydrochloric acid (HCl) mixture. The $SnCl_2$ is present to reduce any thiuram disulfide to the dithiocarbamate and to inhibit oxidation of the dithiocarbamate prior to its decomposition. The generated CS_2 is extracted from the water into hexane during the decomposition process and determined by GC using a Hall detector in the sulfur mode. This procedure has proven to be more sensitive and easier than previous developed colorimetric detection methods. A cleanup method is provided to remove any CS_2 originally present in the wastewater. This cleanup method involves purging of the CS_2 from the sample using a vortex evaporator. The final method is described in Appendix A of this report.

SECTION 2

CONCLUSIONS

CLEANUP

CS_2 is effectively purged from a sample buffered at pH 12.2 using three 10-minute cycles in a vortex evaporator. Methyl t-butyl ether (MTBE) is added to the sample prior to each cycle in the vortex evaporator to aid CS_2 removal. After this CS_2 removal step, the sample can be hydrolyzed to form CS_2 from any dithiocarbamate pesticides present. Disodium dithiocarbonate (DSDTC) formed from CS_2 in the original basic sample does not yield detectable levels of CS_2 upon acidification of the sample.

CHROMATOGRAPHY

A 0.1% SP-1000 on Carbopack C column is suitable for use in the determination and quantification of CS_2. An internal standard suitable for use in this method was not identified.

STABILITY STUDIES

Certain dithiocarbamate pesticides are increasingly unstable in aqueous solution when the pH of that solution is lowered. A pH buffer of 12.2 is necessary for storage and for the CS_2 purging cleanup step to minimize degradation of these dithiocarbamate pesticides. Although long term stability studies were not conducted for the pesticides, preliminary data indicated that many of the dithiocarbamates are not stable in solution even at pH 12.2 for more than a week.

VALIDATION STUDIES

MDLs for the 13 dithiocarbamates studied ranged from 1.1 to 5.2 µg/L. Recoveries for these compounds from reagent water over a concentration range of 10 to 1000 µg/L were consistent on an individual basis. Recoveries of these pesticides at the 50 and 500 µg/L levels from diluted dithiocarbamate wastewater were consistent with those obtained from reagent water. Recoveries of amobam, Busan 40, Busan 85, ferbam, KN-methyl, metham, NaDMDTC, thiram, zineb, and ziram were generally greater than 85 percent. Recoveries of EXD, nabam, and nabonate were consistently lower than 85 percent, presumably due to structural differences or problems with the standards obtained for the

studies. Hydrolysis of three dithiocarbamate polymers, maneb, mancozeb, and polyram, resulted in low yields of CS_2. This was presumably due to impure standard compounds, the high stability of these polymers, or the low solubility of these compounds in water.

SECTION 3

EXPERIMENTAL

Studies were designed to develop a simple, effective method to remove indigenous CS_2 from a water sample prior to dithiocarbamate determination. Attempts were also made to obtain a suitable compound for use as an internal standard for dithiocarbamate determinations. Minimal dithiocarbamate stability studies were conducted to aid in determining optimal pH range for sample storage.

CLEANUP

The cleanup step originally developed for this method involved extraction of the wastewater sample with hexane to remove indigenous CS_2. This step was performed at basic pH before acidification of the sample to effect hydrolysis of the dithiocarbamates to release more CS_2. This cleanup step was found to be reasonably effective, but became tedious and time-consuming when processing large numbers of samples. Two alternative cleanup methods were identified based on the fact that CS_2 is easily purged from water:

- Removal of CS_2 from water using a vortex evaporator
- Removal of CS_2 from water by purging with nitrogen.

Because of the expected ease of sample processing, both of the CS_2 purging cleanup methods were investigated.

Five-milliliter samples of water spiked with CS_2 were placed in 15-mL conical centrifuge tubes. CS_2 concentrations were determined before the samples were used for cleanup method studies; CS_2 concentrations varied from 1 to 4 µg/mL. Each sample was treated with 0.75 g of NaCl to give a 15 percent NaCl solution and then subjected to a 250-mL/min nitrogen flow eluting from a 19-gauge needle. Triplicate samples were purged with nitrogen in this manner. The original sample, as well as samples subjected to one, two, or three 10-minute purges with nitrogen, were extracted with an equal volume of hexane and analyzed by GC-Hall. CS_2 removal using a vortex evaporator was investigated in the same manner. Methyl t-butyl ether (MTBE), 2 mL, was added to each sample and the samples were placed in the vortex evaporator for 10 minutes. The vortex evaporator was operated with the temperature set at 30°C, the vacuum set at 29 to 30 inches Hg, and a moderately fast vortexing rate setting of 4.5. Samples were subjected to one, two, or three 10-minute intervals in the vortex evaporator, with MTBE being added prior to each interval. Samples were extracted with an equal volume of hexane and analyzed by GC-Hall. The

above mentioned vortex evaporator CS_2 removal experiment was conducted in both plastic and glass conical centrifuge tubes.

The above described studies were conducted in a 0.1 M solution of dibasic sodium phosphate (pH 9). This pH value was used originally to avoid the formation of disodium dithiocarbonate (DSDTC) from CS_2, which occurs more readily as the pH of the CS_2 solution is increased. It was expected that DSDTC might form CS_2 when the sample was readjusted to a more acidic pH range. As method validation progressed, it became apparent that some of the dithiocarbamate pesticides were unstable at pH 9, especially at low concentration levels. For this reason, CS_2 removal studies were repeated using CS_2 solutions in 0.1 M tribasic sodium phosphate solutions (pH 12.2). These studies were again done in triplicate using 1000 µg/L solutions of CS_2. The samples were run through three 10-minute cycles in the vortex evaporator, and then extracted with equal volumes of hexane prior to analysis by GC-Hall. Triplicate samples were also run through the hydrolysis step of the procedure to determine if any CS_2 was being released by DSDTC formed in the original basic solution.

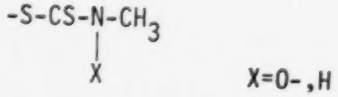
CHROMATOGRAPHY

A 0.1% SP-1000 on 80/100 mesh Carbopack C column conbined with a Hall detector operated in the sulfur mode was used for all CS_2 determinations. This combination was previously found to be suitable for this purpose.

Two compounds, methyl sulfide and ethyl sulfide, were examined to see if they would be suitable for use as internal standards. Hexane solutions of these two compounds at varying concentrations were analyzed to determine if they yielded acceptable peak shapes and if they eluted acceptably close to the CS_2 peak.

STABILITY STUDIES

Although some of the dithiocarbamate pesticides seemed to be relatively stable in pH 9 buffer, others were not stable at this pH value. This instability became especially obvious when compounds with the following structures were examined:



X=O-,H

It became necessary to examine compound stability at higher pH values to determine if the dithiocarbamate pesticides were more stable at these higher pH values. One of the dithiocarbamate compounds with this structure, Busan 40, was found to be particularly unstable in pH 9 buffer. This instability became more pronounced as the Busan 40 concentration in the buffer was lowered. Duplicate 5-mL samples of Busan 40 at the 10 µg/L concentration level were prepared in pH 9, 10, 11, and 12.2 phosphate

buffers. These samples were analyzed using the dithiocarbamate method, and Busan 40 recoveries were calculated.

Long term stability for the dithiocarbamate compounds was not studied during this task.

VALIDATION STUDIES

The MDLs for the dithiocarbamate pesticides were determined by analyzing seven replicate reagent water samples with the specific dithiocarbamate pesticide spiked at the 10 µg/L level. The procedure used was that described in Appendix A. The recovery of dithiocarbamate pesticide was calculated from the amount of CS_2 detected in the hexane extract, which in turn was determined by external standard calibration. The MDLs were then calculated from the dithiocarbamate recovery data.

Reagent water was also spiked in duplicate with the individual dithiocarbamate pesticides at the 10, 50, 100, 500, and 1000 µg/L levels. Recoveries of these dithiocarbamates were determined as previously described. Analytical curves were generated by plotting the amount of dithiocarbamate spiked into the samples versus the calculated amount recovered from the samples.

A wastewater sample was obtained from a manufacturer of a dithiocarbamate. Triplicate samples of this wastewater were analyzed prior to the cleanup step, after the cleanup step, and after the hydrolysis step to determine indiginous CS_2 levels as well as dithiocarbamate concentration levels in the wastewater. The wastewater contained very high levels of dithiocarbamates. For this reason, in accordance with the recommendation of the project officer, it was diluted 1000:1 with Columbus secondary POTW effluent prior to use in validation studies. Seven aliquots of this diluted wastewater were then analyzed to determine background dithiocarbamate levels. The diluted wastewater was then spiked at the 50 and 500 µg/L levels with the individual dithiocarbamate pesticides and analyzed. Seven replicate extractions were performed at each concentration level. Recoveries of dithiocarbamates, corrected for background dithiocarbamate levels, were then calculated as previously described.

Three of the dithiocarbamate pesticides, mancozeb, maneb, and polyram, are polymers. These compounds are not detectably soluble in water or any organic solvents. These compounds also do not readily form dispersions. Validation studies could not be performed for these compounds. Although it is unlikely that these compounds would be present dissolved in a wastewater, it must be recognized that they could be present adsorbed to any particulate associated with the wastewater. For this reason, an attempt was made to determine the hydrolysis efficiency of these compounds using the conditions described in Appendix A. Known quantities, approximately 0.1 mg, of these compounds were placed in 5 mL of pH 12.2 buffer and hydrolyzed as described in the dithiocarbamate analysis method. The resultant CS_2 evolved was quantified by GC-Hall after extraction with hexane. These analyses were performed in triplicate.

SECTION 4

RESULTS AND DISCUSSION

CLEANUP

Studies conducted in pH 9 buffer indicated that the optimum cleanup method consisted of purging of the CS_2 from the aqueous media in a vortex evaporator. CS_2 removal data comparing CS_2 purging efficiency from water using nitrogen purging or a vortex evaporator are given in Table 1. Use of a vortex evaporator to remove the CS_2 proved to be slightly more efficient than nitrogen purging. Presumably dispersion of the nitrogen gas from the 19 gauge needle through the sample was not sufficient for effective CS_2 removal. Detectable levels of CS_2 were removed after three 10-minute cycles in the vortex evaporator. Regardless of the method used, CS_2 was not removed as quickly as expected. It was postulated that the plastic tubes were responsible for the retention of some of the CS_2. Data obtained from identical studies conducted using glass conical centrifuge tubes instead of plastic tubes indicated this to be the case. These data are also given in Table 1. When using glass centrifuge tubes, detectable levels of CS_2 were removed after only one 10-minute cycle in the vortex evaporator.

TABLE 1. CS_2 RECOVERY EFFICIENCIES FROM pH 9 BUFFER[f]

Cycle[a]	Percent CS_2 Recovered Using Given Method[b]		
	Nitrogen Purge[c]	Vortex Evaporator[c]	Vortex Evaporator[d]
1	12 (1.0)	9.6 (0.4)	ND
2	8.0 (0.5)	5.3 (0.5)	ND
3	6.6 (0.2)	ND[e]	ND

(a) A cycle is defined as one 1-minute purge with nitrogen or one 10-minute period in the vortex evaporator.
(b) Data are the averages of triplicate analyses; standard deviation is given in parenthesis.
(c) Plastic centrifuge tubes used.
(d) Glass centrifuge tubes used.
(e) ND = Below detection limits.
(f) Original CS_2 concentrations in the pH 9 buffer varied from 1 to 4 µg/mL.

In order to ensure storage stability of some of the dithiocarbamate pesticides, it became necessary to perform the cleanup step in pH 12.2 buffer as opposed to pH 9 buffer. CS_2 removal studies were performed to ascertain if CS_2 was adequately removed at these higher pH levels. When pH 12.2 buffer solutions containing approximately 1000 µg/L levels of CS_2 were run through the cleanup procedure, no CS_2 was detected. After hydrolysis, no detectable additional CS_2 was produced. Detection limits for CS_2 were approximately 3 µg/L in the buffer samples. Apparently upon hydrolysis of the samples, any DSDTC present does not produce CS_2. Subsequently, pH 12.2 buffer solutions spiked at the 10 µg/L levels with dithiocarbamates yielded recoveries of greater than 85 percent. In fact, the increase in the pH of the matrix was shown to increase the stability of some of the dithiocarbamates such as Busan 40 in aqueous media. It was determined that the cleanup method developed using the vortex evaporator is suitable for use with samples at pH 12.2. The cleanup method effectively removed CS_2 even at high concentration levels such as 1000 µg/L while still allowing accurate determination of dithiocarbamates present at the low µg/L level.

CHROMATOGRAPHY

Methyl sulfide and ethyl sulfide were not suitable for use as internal standard compounds. Methyl sulfide eluted slightly before CS_2, but the resultant peak tailed badly. This made integration of both the methyl sulfide and the CS_2 peaks difficult. It is possible that methyl sulfide still might be used as an internal standard compound if capillary GC columns were used instead of a packed GC column. Ethyl sulfide was not detected under the GC conditions used for CS_2 determinations. Presumably it eluted with the hexane solvent peak and presumably is not volatile enough for use in this analysis method. An internal standard appropriate for use in this analysis method was not identified.

STABILITY STUDIES

Stability studies indicated that dithiocarbamate compounds such as Busan 40 are more stable when the pH of the matrix is raised. Recoveries of Busan 40 from 10 µg/L solutions adjusted to pH values of 9, 10, 11, and 12.2 are given in Table 2. The recovery of Busan 40 was dramatically increased as the pH of the solution was increased. Validation studies for all of the dithiocarbamate pesticides were conducted in pH 12.2 buffer (0.1 M tribasic sodium phosphate).

Although formal stability studies were not conducted for all of the dithiocarbamate pesticides, standard solutions were generally prepared just prior to their use. In a few isolated cases, standard solutions were used that had been stored for one to two weeks in a refrigerator. In all cases, unexpectedly low recoveries for the dithiocarbamates were obtained, and the studies had to be repeated with new standard solutions. Although this information is preliminary, it does indicate that instability problems might be encountered if long term storage of samples and standard solutions is attempted.

TABLE 2. RESULT OF BUSAN 40 pH STABILITY STUDIES

pH	Percent Recovery[a]
9	38, 41
10	59, 55
11	62, 75
12.2	88 (1.4)[b]

(a) Results from duplicate analyses.
(b) Average of seven replicate analyses; standard deviation given in parentheses.

VALIDATION STUDIES

Results from the MDL studies are given in Table 3. Calculated MDL values were in the range of 1.1 to 5.2 µg/L. Recoveries for 10 of the dithiocarbamates from reagent water were also greater than 85 percent over a concentration range of 10 to 1000 µg/L. Recoveries of EXD, nabam, and nabonate were less than 85 percent at all concentration levels. Analytical curve data are given in Table 4. The resultant analytical curves are shown in Figures 1-13.

The diluted dithiocarbamate wastewater contained low levels of dithiocarbamate, 4.5 to 6.2 µg/L, depending upon the dithiocarbamate analyzed. Recoveries of the dithiocarbamates from the diluted wastewater were in most cases greater than 85 percent. Method validation data for the dithiocarbamate pesticides in wastewater are given in Table 5. Recoveries for EXD, nabam, and nabonate were less than 85 percent at both the 50 and 500 µg/L concentration levels. Slightly low recoveries of 84 percent and 82 percent were calculated at the 500 µg/L level for metham and the 500 µg/L level for thiram, respectively.

Examination of the structures of EXD and nabonate indicate that these two compounds are probably more susceptible to formation of hydrolysis products other than CS_2, therefore accounting for the low recoveries achieved. These two compounds have structures that deviate from the normal dithiocarbamate structure. Both pesticides yielded relatively constant low recoveries regardless of the concentration level or matrix used, indicating that the low recoveries are not caused by a concentration-related instability. The low recoveries encountered when studying nabam can not be easily explained. The literature does not indicate any instability of nabam in the presence of water, heat, or light. Recoveries of nabam were again consistently low regardless of the concentration level or matrix used. A nabam standard to use for recovery studies was only available from one source. A standard of a structurally similar dithiocarbamate, amobam, obtained from this same source yielded lower recoveries than that obtained from a second source. It was concluded that the standard itself was very likely not as pure as the source specified.

TABLE 3. RESULTS OF METHOD DETECTION LIMIT STUDY FOR DITHIOCARBAMATE PESTICIDES IN REAGENT WATER

Compound	Amount Spiked, µg/L	Amount Found in Given Spiked Replicate, µg/L								SD[a]	MDL[b]	Average Percent Recovery
		Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average			
Amobam	10	8.9	9.4	8.7	9.5	9.4	9.6	9.4	9.3	0.34	1.1	93
Busan 40	10	8.0	7.1	7.8	11	9.3	8.5	9.4	8.7	1.3	4.1	87
Busan 85	10	11	10	10	11	10	11	9.7	10	0.58	1.8	100
EXD	10	6.9	9.1	7.9	9.3	5.5	5.5	5.7	7.1	1.7	5.3	71
Ferbam	10	11	13	11	9.7	11	10	10	11	1.1	3.5	110
KN-Methyl	10	8.6	10	8.3	8.9	8.3	8.6	7.4	8.6	0.78	2.5	86
Metham	10	9.8	8.7	8.6	8.7	9.7	10	11	9.5	0.89	2.8	95
Nabam	10	2.9	3.7	4.5	4.1	3.8	4.0	3.9	3.8	0.49	1.5	38
Nabonate	10	5.0	5.5	5.7	5.5	5.4	5.2	4.9	5.3	0.29	0.9	53
NaDMDTC	10	11	9.6	12	11	11	10	9.6	11	0.89	2.8	110
Thiram	10	8.0	8.0	9.7	9.6	9.0	9.4	8.9	8.9	0.71	2.2	89
Zineb	10	8.0	9.2	7.9	7.6	10	9.6	11	9.0	1.3	4.1	90
Ziram	10	7.5	8.6	8.7	8.3	9.8	11	11	9.3	1.4	4.4	93

(a) SD = Standard Deviation.
(b) MDL = Method Detection Limit.

TABLE 4. RESULTS OF ANALYTICAL CURVE STUDY FOR DITHIOCARBAMATE PESTICIDES IN REAGENT WATER

Compound	Amount Found at Given Spike Level, µg/L				
	10(a)	50(b)	100(b)	500(b)	1000(b)
Amobam	9.3 (0.33)	45,44	84,94	500,450	1100,960
Busan 40	8.8 (1.4)	44,45	86,84	530,520	930,880
Busan 85	10 (0.43)	45,53	97,96	570,550	800,1100
EXD	7.1 (1.7)	30,29	56,62	310,300	610,600
Ferbam	11 (0.93)	42,43	82,90	460,450	900,930
KN-Methyl	8.6 (0.87)	53,55	85,87	510,430	1000,870
Metham	9.6 (1.0)	47,47	94,85	450,530	970,920
Nabam	3.8 (0.51)	23,25	41,45	320,330	630,660
Nabonate	5.3 (0.28)	32,29	73,73	310,290	620,660
NaDMDTC	11 (0.88)	46,43	100,100	450,430	950,920
Thiram	8.9 (0.71)	43,43	100,83	430,410	1100,750
Zineb	9.1 (1.3)	56,53	89,85	460,450	880,840
Ziram	9.3 (1.5)	54,55	92,86	450,490	990,1000

(a) Average of seven replicate analyses; standard deviation given in parentheses.
(b) Results of duplicate analyses.

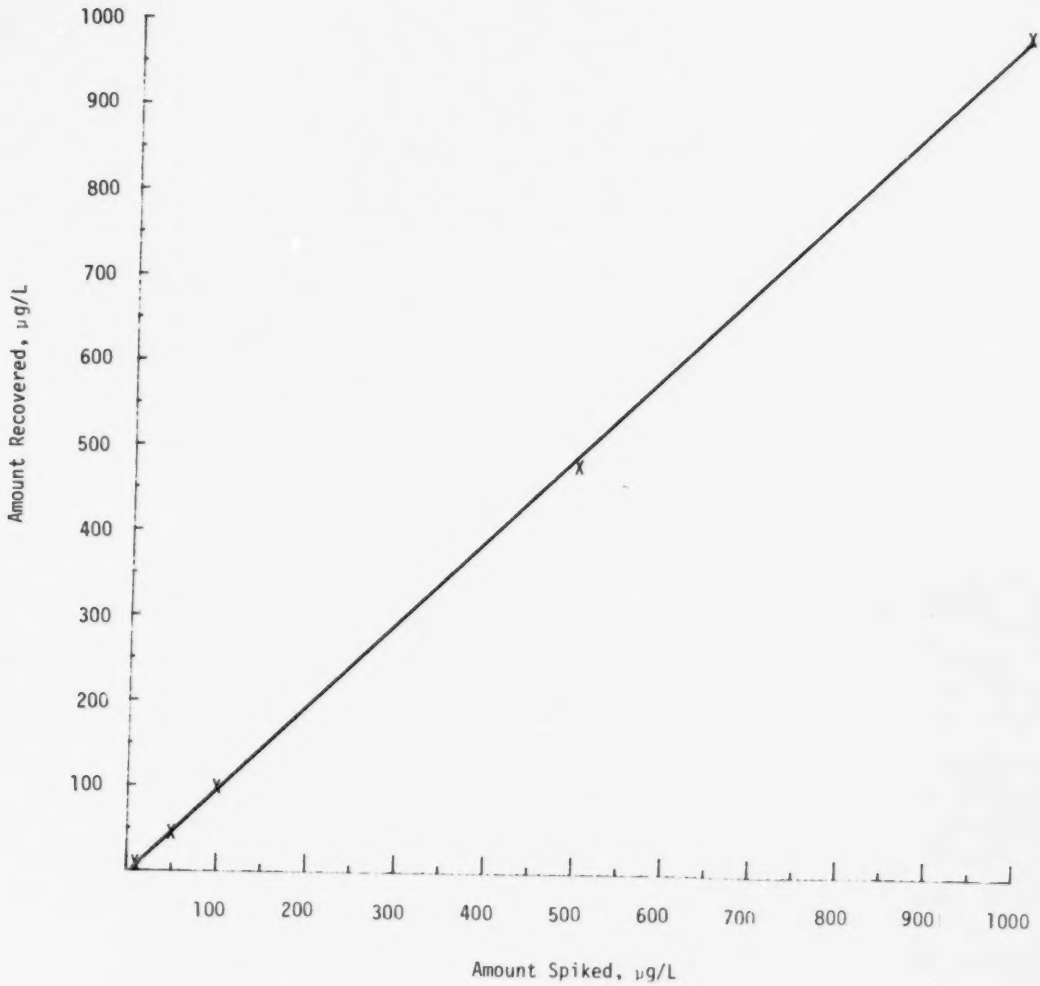


FIGURE 1. ANALYTICAL CURVE FOR AMOBAM

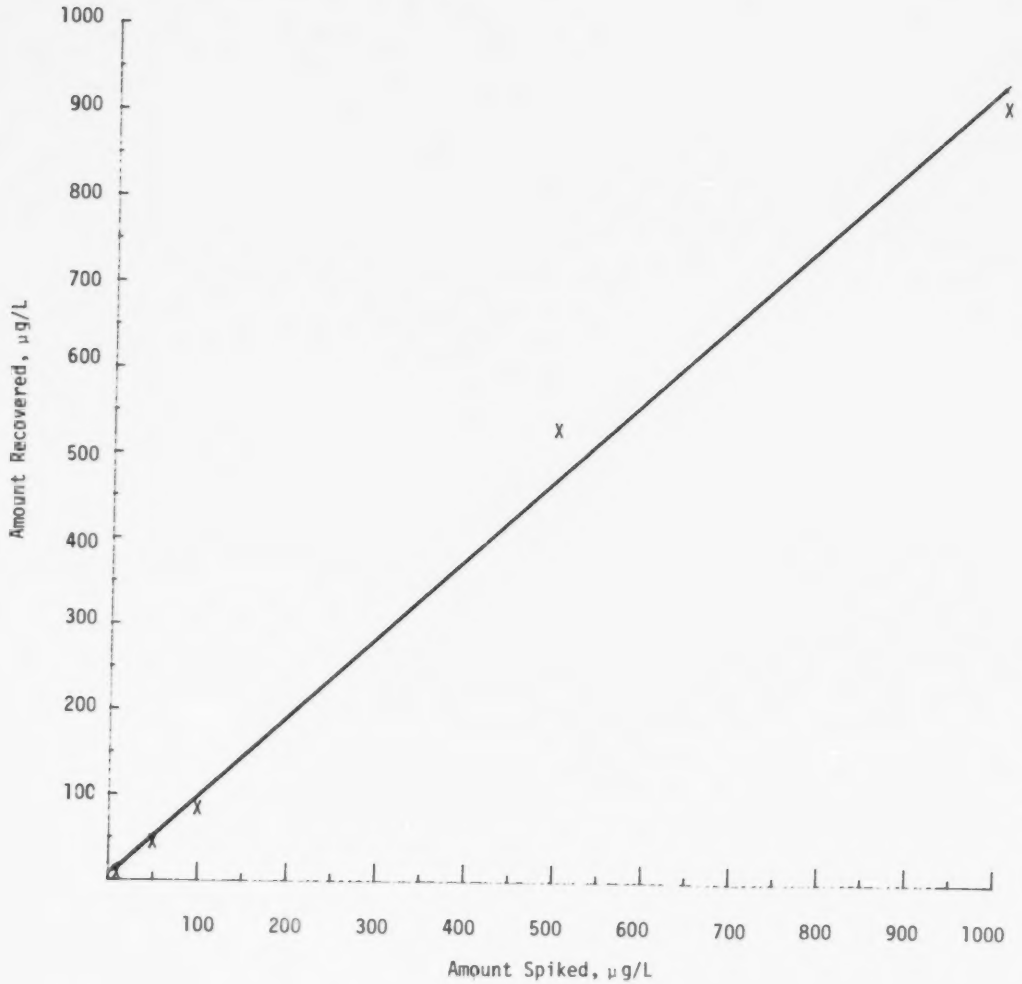


FIGURE 2. ANALYTICAL CURVE FOR BUSAN 40

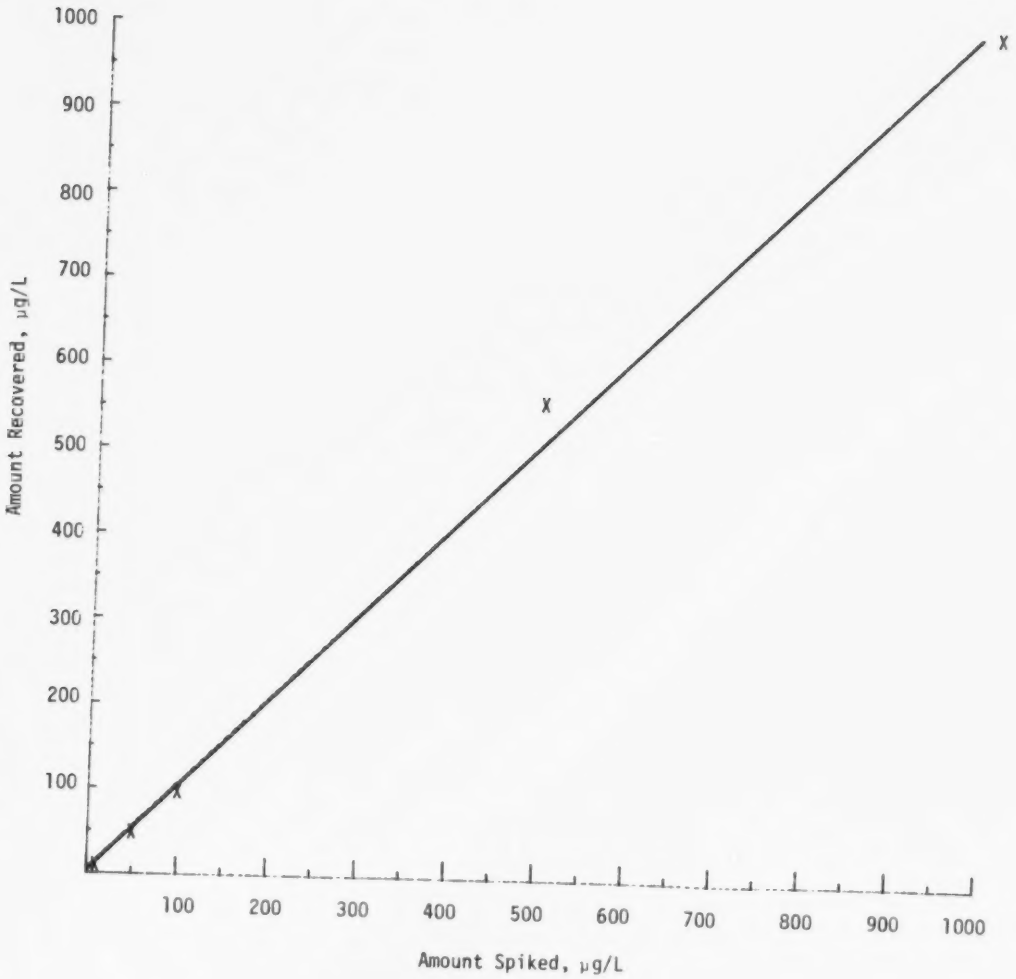


FIGURE 3. ANALYTICAL CURVE FOR BUSAN 85

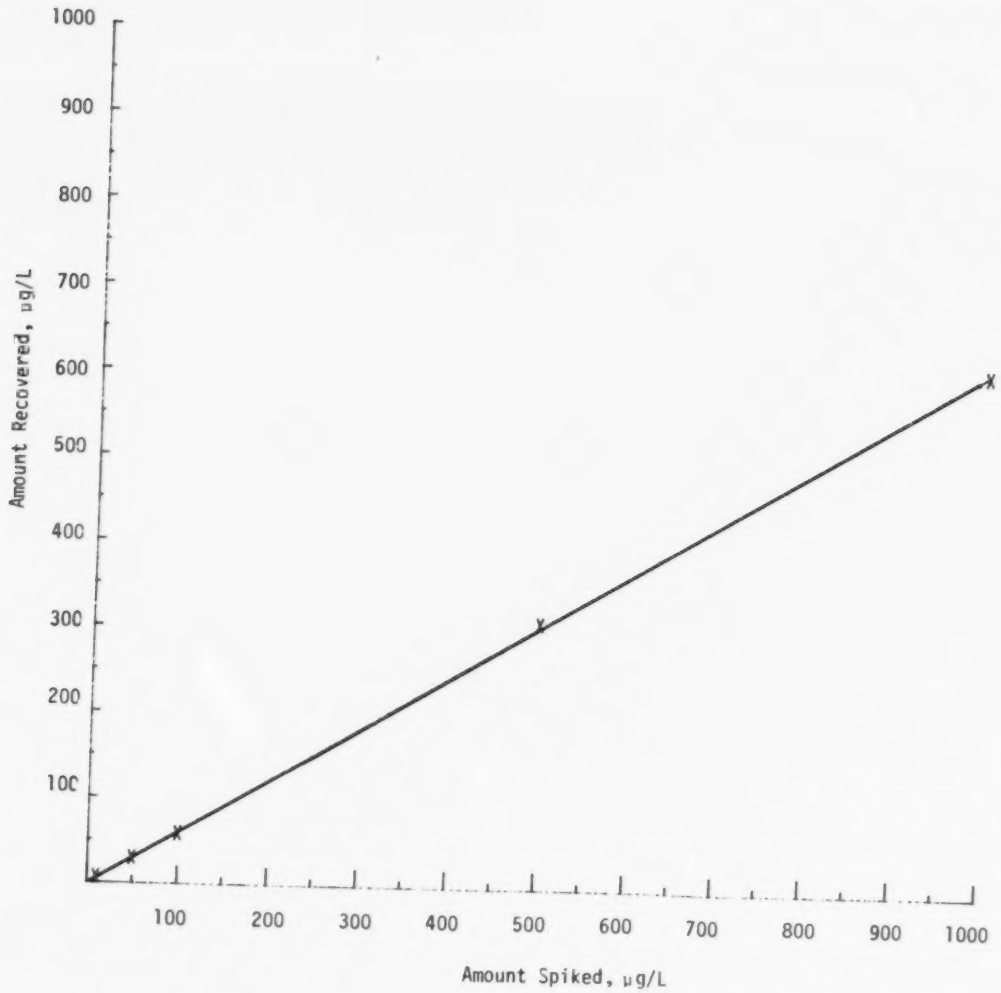


FIGURE 4. ANALYTICAL CURVE FOR EXD

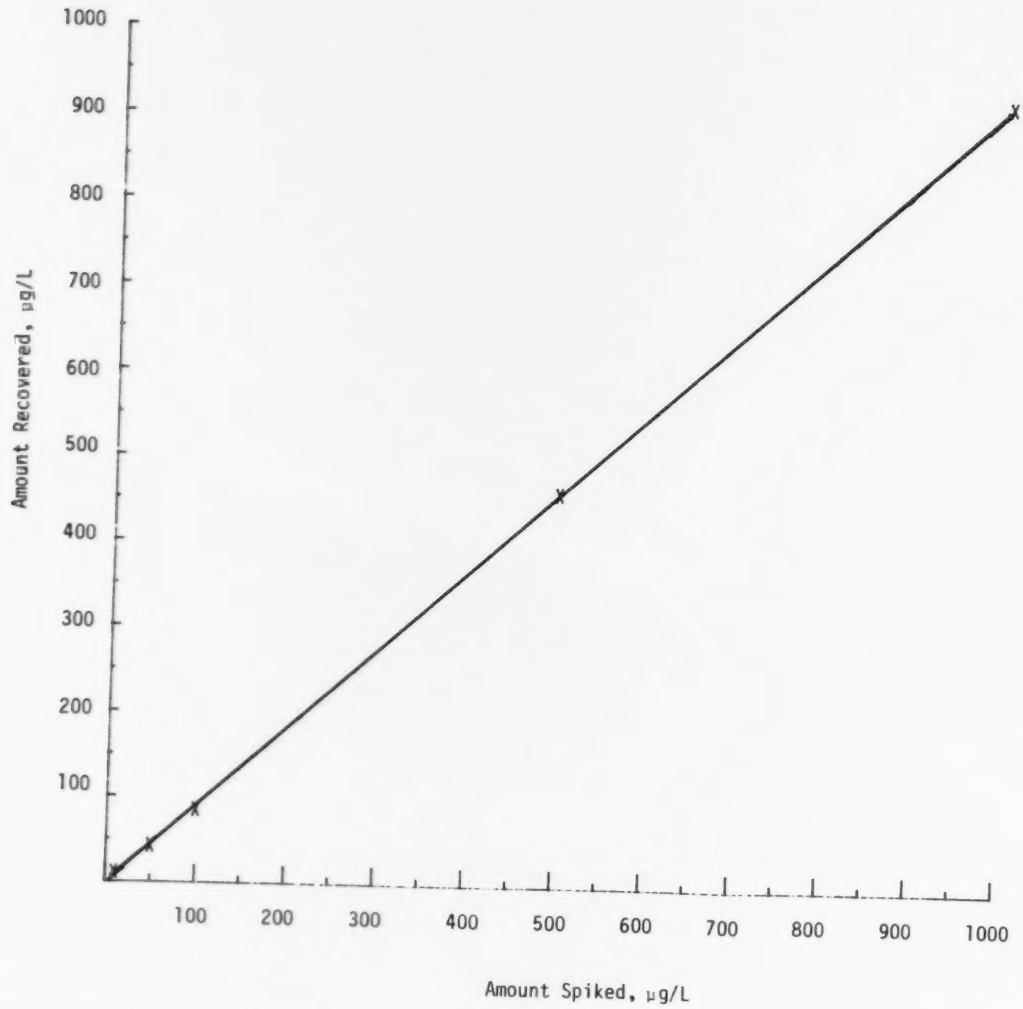


FIGURE 5. ANALYTICAL CURVE FOR FERBAM

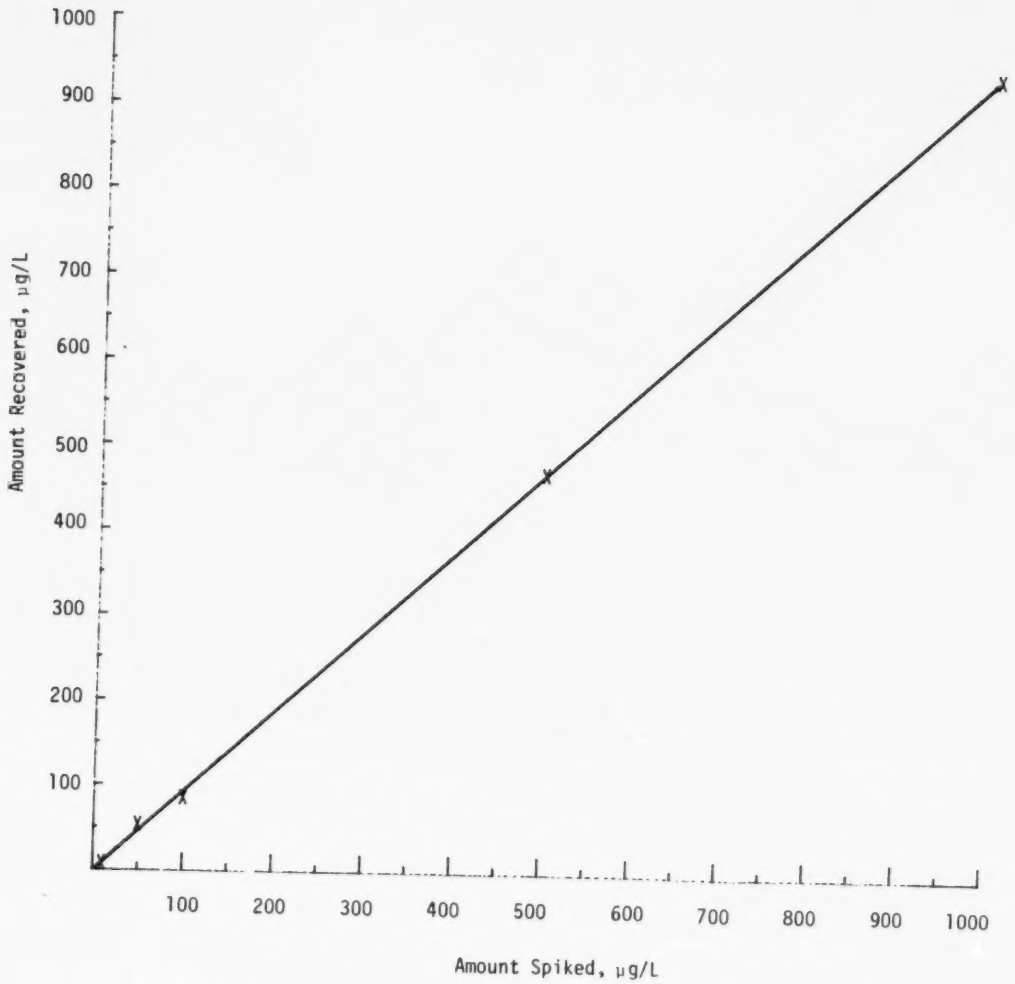


FIGURE 6. ANALYTICAL CURVE FOR KN-METHYL

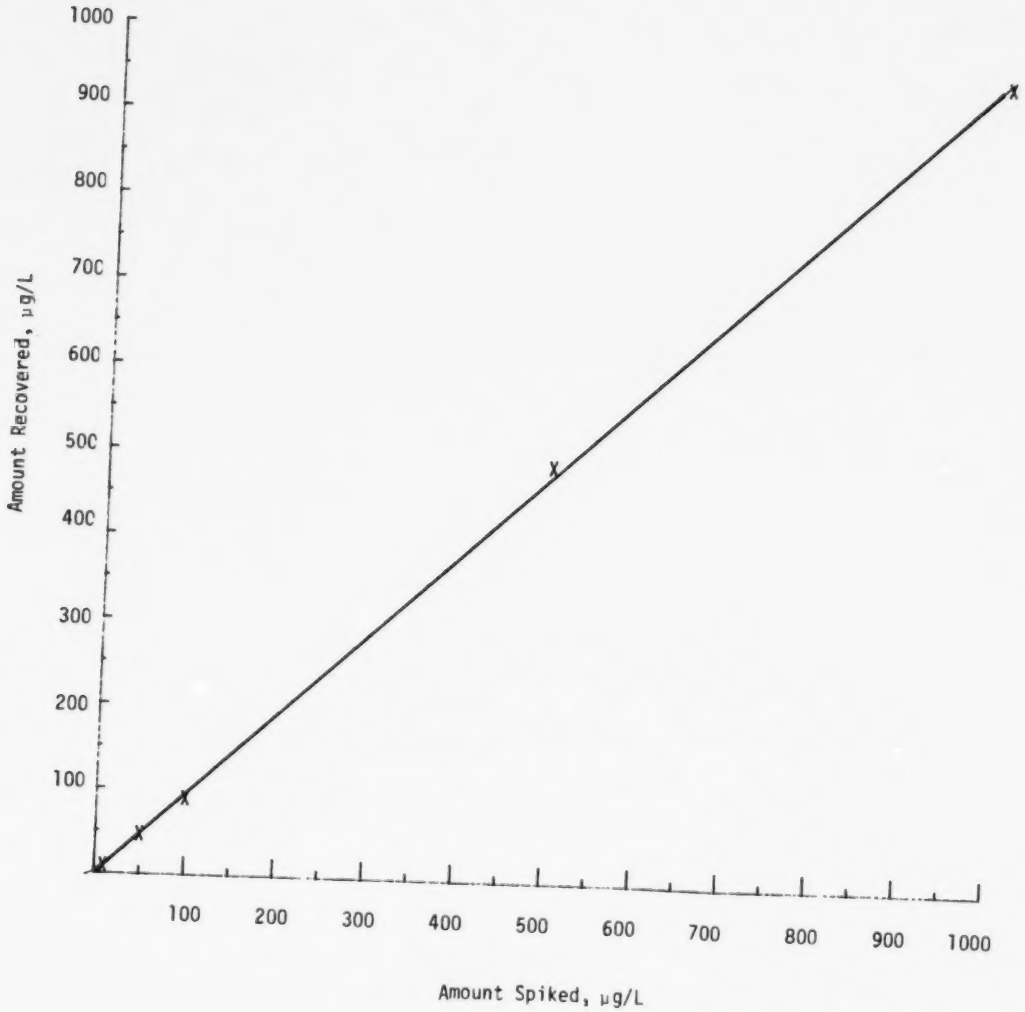


FIGURE 7. ANALYTICAL CURVE FOR METHAM

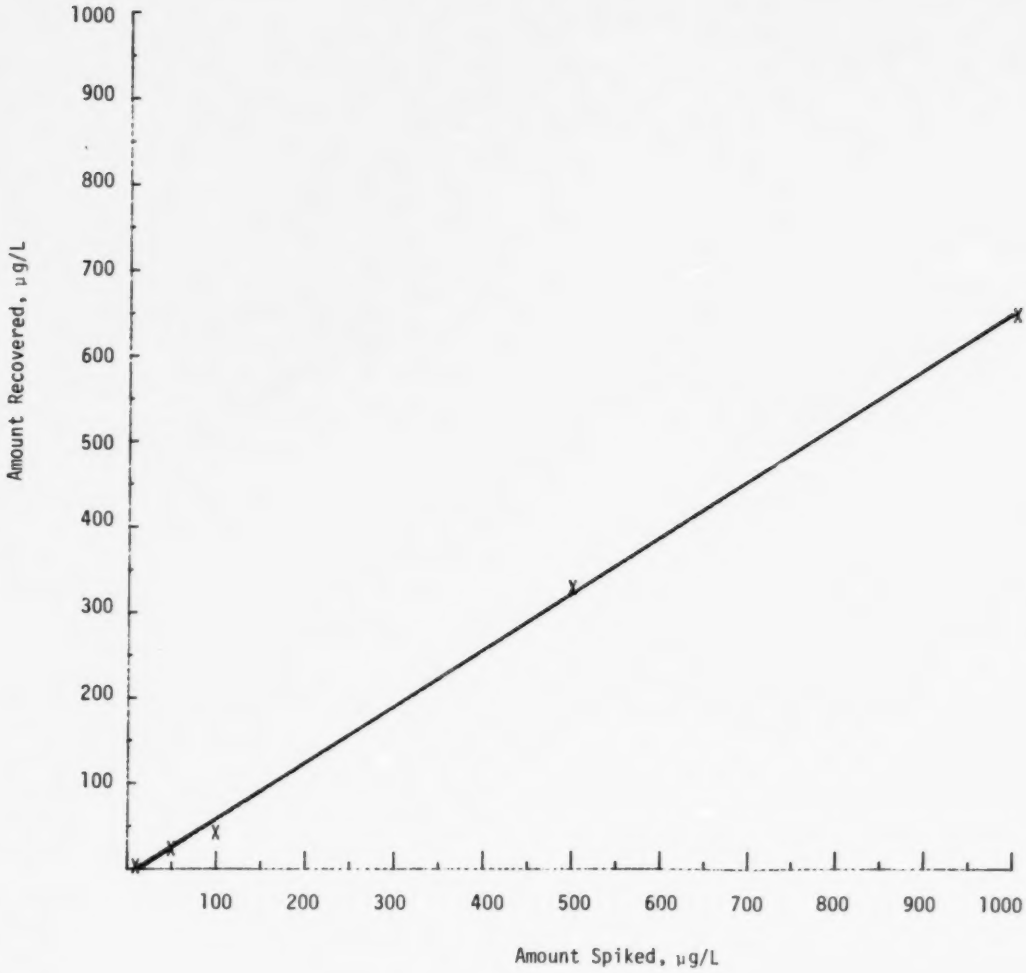


FIGURE 8. ANALYTICAL CURVE FOR NABAM

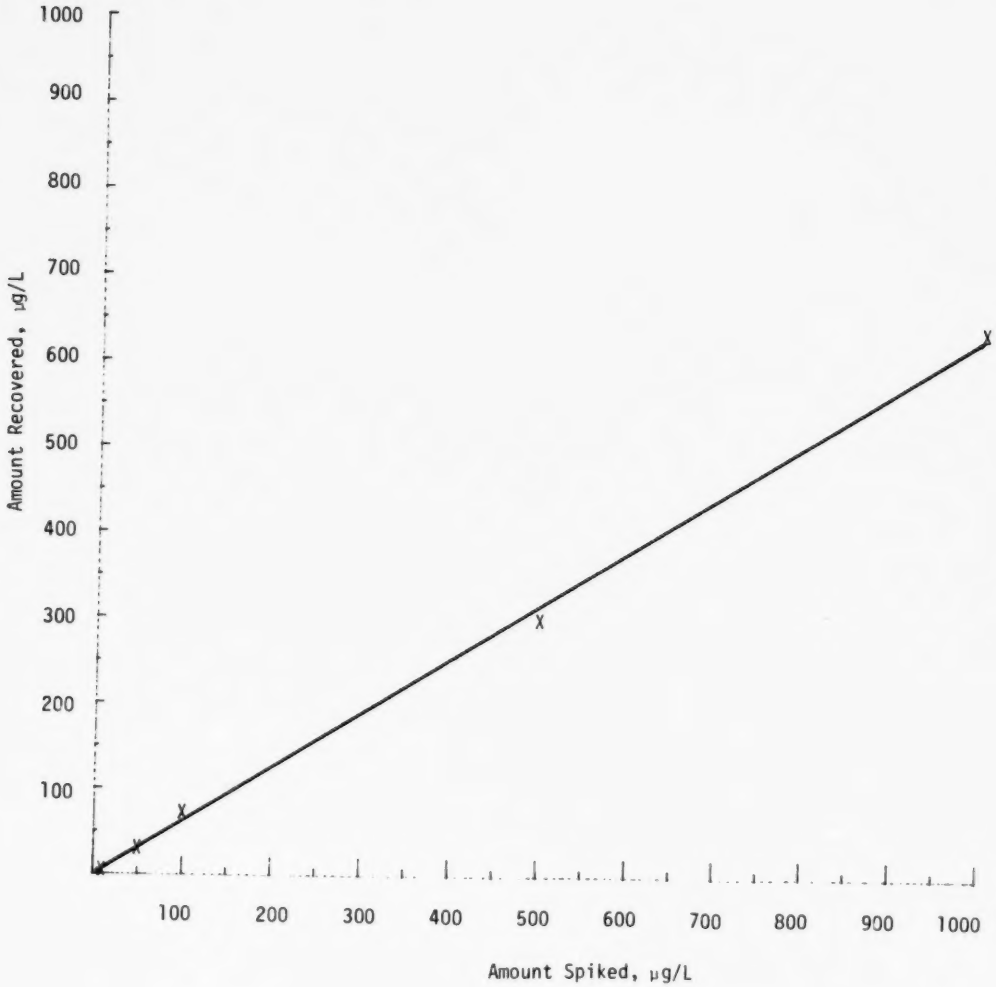


FIGURE 9. ANALYTICAL CURVE FOR NABONATE

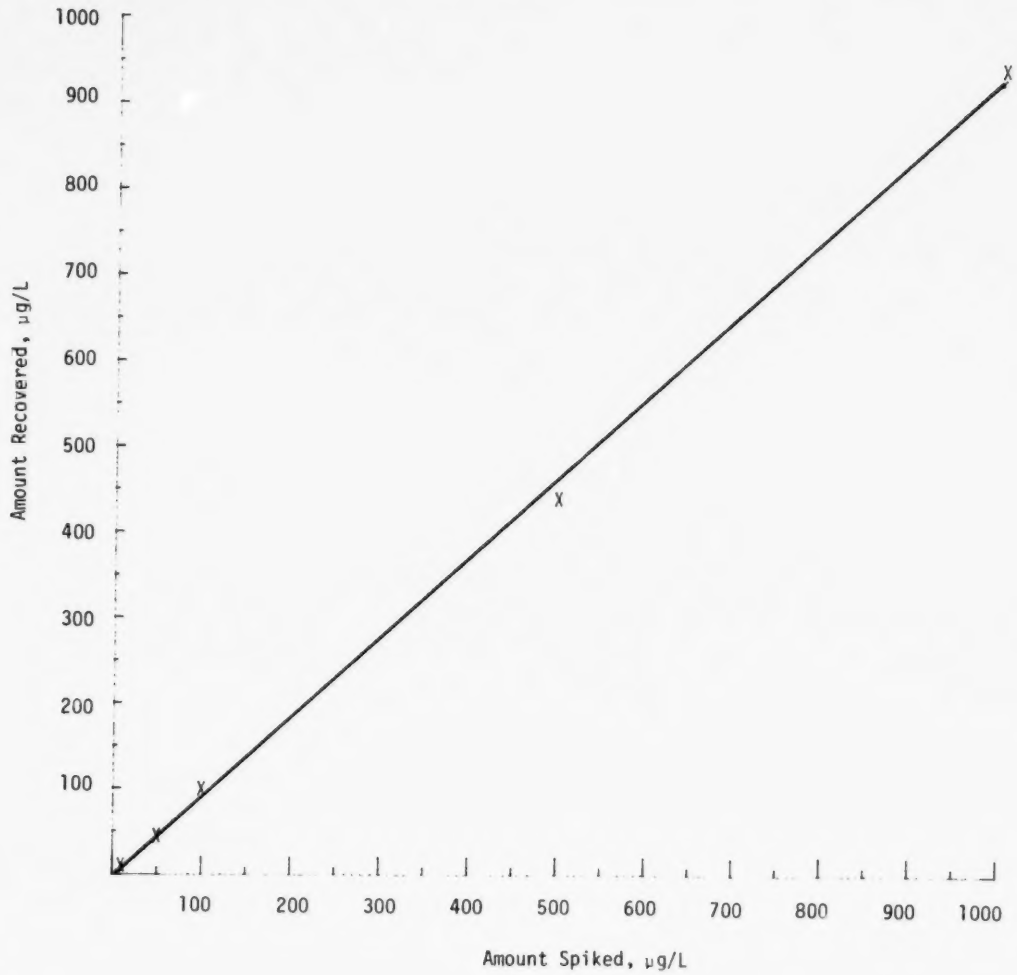


FIGURE 10. ANALYTICAL CURVE FOR NaDMDTC

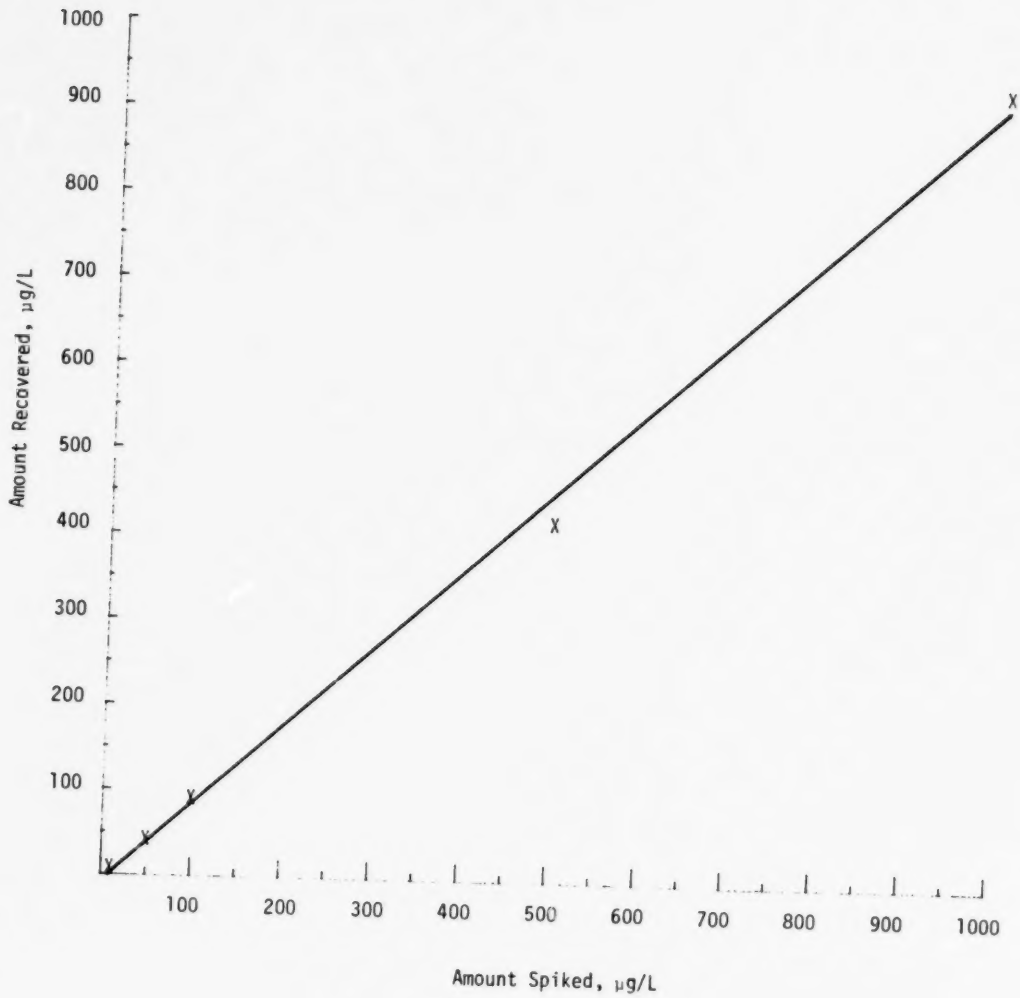


FIGURE 11. ANALYTICAL CURVE FOR THIRAM

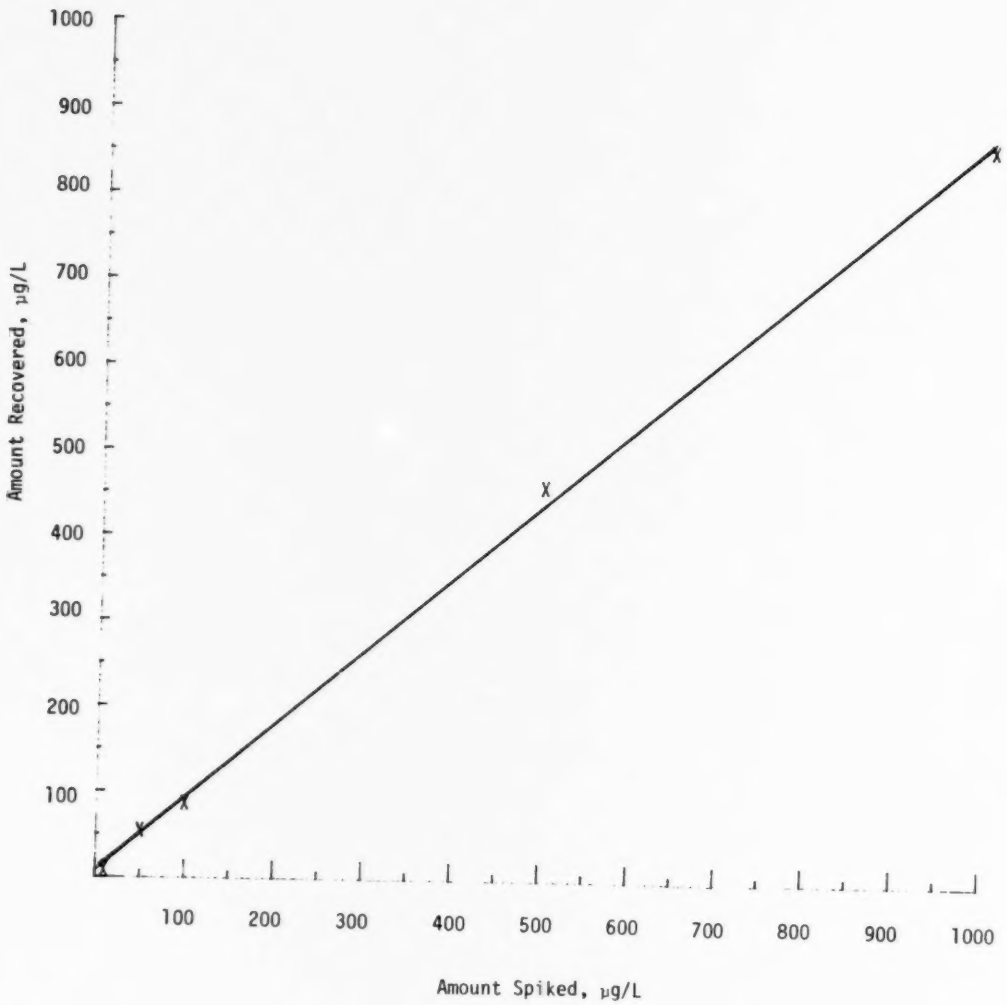


FIGURE 12. ANALYTICAL CURVE FOR ZINEB

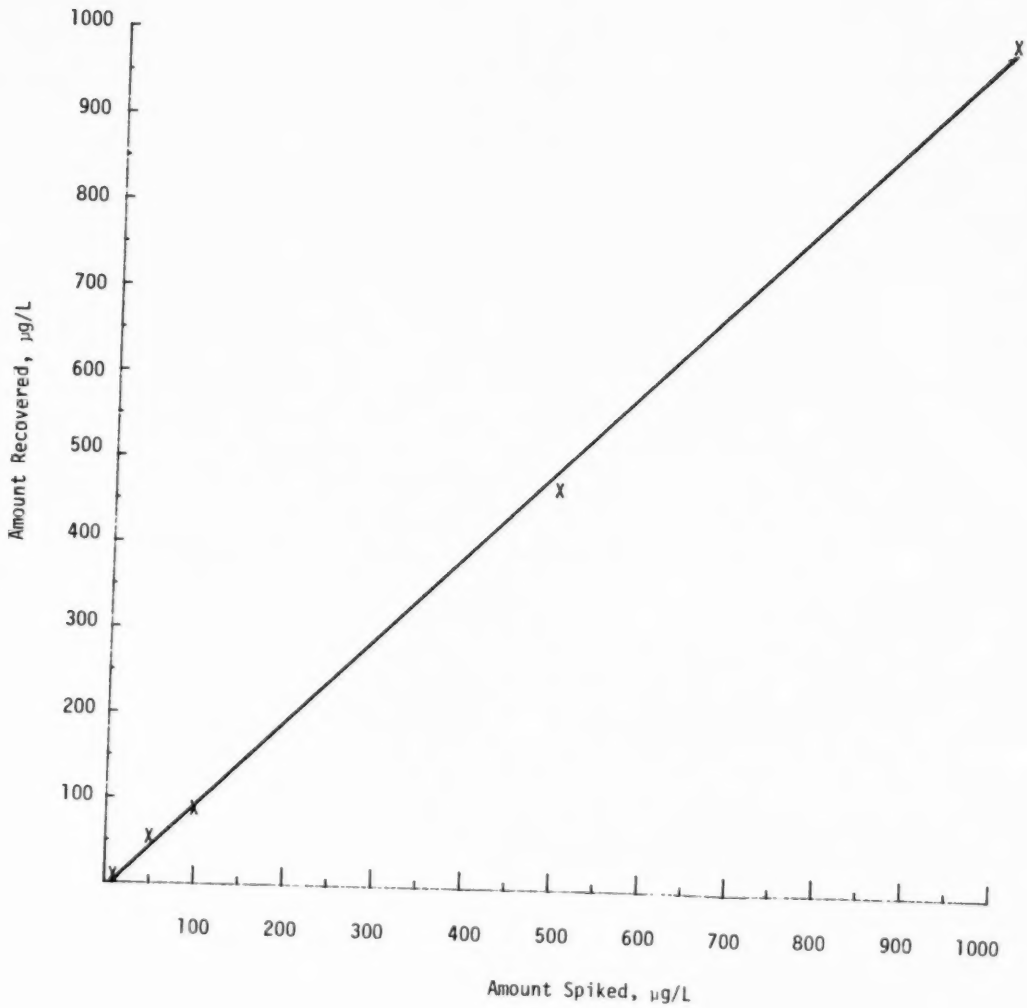


FIGURE 13. ANALYTICAL CURVE FOR ZIRAM

TABLE 5. RESULTS OF METHOD VALIDATION STUDY FOR DITHIOCARBAMATE PESTICIDES IN WASTEWATER

Compound	Background Level, µg/L	Amount Spiked, µg/L	Amount Found in Given Spiked Replicate, µg/L(c) Rep. 1	Rep. 2	Rep. 3	Rep. 4	Rep. 5	Rep. 6	Rep. 7	Average	SD(a)	RSD, %(b)	Average Percent Recovery
Amobam	4.6	50	48	48	48	43	47	43	39	45	3.5	7.8	90
	4.6	500	450	440	420	470	500	450	540	470	41	8.7	93
Busan 40	6.6	50	52	49	55	49	58	58	56	54	3.9	7.2	110
	6.6	500	520	500	510	510	550	530	450	510	31	6.1	100
Busan 85	5.9	50	58	57	56	55	59	58	50	56	3.0	5.5	110
	5.9	500	530	530	500	510	520	520	510	510	10	2.0	100
EXD	4.5	50	34	37	34	35	36	41	32	36	2.7	7.5	71
	4.5	500	380	390	370	390	370	390	380	380	9.1	2.4	76
Ferbam	5.2	50	44	44	47	48	48	48	50	47	2.2	4.8	94
	5.2	500	540	550	530	560	540	560	550	540	9.9	1.8	110
KN-Methyl	5.4	50	46	41	44	44	45	44	50	45	2.7	6.1	90
	5.4	500	460	440	430	440	460	440	440	440	11	2.5	89
Metham	6.2	50	53	51	56	53	59	52	52	53	2.8	5.2	110
	6.2	500	430	440	430	370	410	410	450	420	25	5.9	84
Nabam	4.8	50	31	33	33	31	27	33	31	31	2.0	6.6	62
	4.8	500	400	310	330	310	260	340	340	320	42	13	65
Nabonate	6.1	50	25	35	32	33	33	36	35	33	3.8	11	66
	6.1	500	300	320	310	250	260	270	230	280	33	12	56
NaDMDTC	5.4	50	53	51	53	54	56	53	54	53	1.3	2.5	110
	5.4	500	550	540	560	530	560	500	520	540	23	4.2	110
Thiram	4.5	50	44	46	43	45	43	45	46	44	1.3	2.9	89
	4.5	500	410	410	410	410	400	420	380	410	14	3.4	82
Zineb	5.2	50	43	45	43	43	46	45	42	44	1.5	3.4	87
	5.2	500	360	400	470	460	430	460	450	430	41	9.4	86
Ziram	5.7	50	59	55	53	50	49	44	42	50	5.9	12	100
	5.7	500	450	420	660	440	430	410	540	480	89	19	95

(a) SD = Standard Deviation.
(b) RSD, % = Percent Relative Standard Deviation.
(c) Corrected for background level.

Hydrolysis efficiencies of the three polymeric dithiocarbamates, mancozeb, maneb, and polyram, were not as high as expected. Recoveries of CS_2 from these three compounds after hydrolysis are given in Table 6. CS_2 was not detected upon hydrolysis of 0.1 mg samples of polyram. Hydrolyses of mancozeb and maneb yielded average CS_2 recoveries of 36 and 34 percent, respectively. The purity of the standards used was assumed to be good, but could not be definitely established. Because these compounds are polymers, the combination of their high stability and low solubility in water might lead to these low recoveries.

TABLE 6. RECOVERIES FROM POLYMER HYDROLYSIS STUDIES

Compound	Percent Recovery[a]
Mancozeb	36 (3.5)
Maneb	34 (2.1)
Polyram	ND[b]

(a) Results are averages of triplicate analyses starting with approximately 0.1 mg of polymer; standard deviation is given in parentheses.
(b) ND = Not detected.

APPENDIX A

THE DETERMINATION OF DITHIOCARBAMATES PESTICIDES
IN WASTEWATER AS CARBON DISULFIDE BY
GAS CHROMATOGRAPHY

METHOD 630.1

1. SCOPE AND APPLICATION

1.1 This method covers the determination of certain dithiocarbamates pesticides after conversion to carbon disulfide. The following parameters can be determined by this method:

Parameter	CAS. No.
Amobam	3566-10-7
Busan 40	51026-28-9
Busan 85	128-03-0
EXD	502-55-6
Ferbam	14484-64-1
KN Methyl	137-41-7
Metham	137-42-8
Nabam	142-59-6
Nabonate	138-93-2
Sodium dimethyldithiocarbamate	128-04-1
Thiram	137-26-8
Zineb	12122-67-7
Ziram	137-30-4

1.2 The compounds are decomposed to form carbon disulfide (CS_2) and the total dithiocarbamate concentration is measured from the amount of CS_2 produced by acid hydrolysis. Unless the sample can be otherwise characterized, all results are reported as Ziram.

1.3 This is a total residue gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. Any

modification of this method beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.4 The method detection limits (MDLs, defined in Section 14) for the parameters listed in Section 1.1 are listed in Table 1. The MDLs for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. SUMMARY OF METHOD[1]

2.1 A measured volume of sample, 5 mL, is digested with acid to yield CS_2 by hydrolysis of the dithiocarbamate moiety. The evolved CS_2 is extracted from water into hexane. Gas chromatographic conditions are described which permit the separation and measurement of CS_2 in the extract by gas chromatography with a Hall detector in the sulfur mode.

2.2 This method provides a cleanup procedure involving purging of any indigenous CS_2 from the sample at pH 12-13. This procedure is performed using a vortex evaporator.

3. INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.5.

3.1.1 Glassware must be scrupulously cleaned[2]. Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water, drain dry, and heat in an oven or muffle furnace at 400°C for 15-30 minutes. Do not heat volumetric ware. Some thermally stable materials such as PCBs may not be eliminated by this treatment. Thorough rinsing with acetone and pesticide quality hexane may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Carbon disulfide may be a direct interferent in wastewaters. This method includes procedures to purge CS_2 from the wastewater prior to acid hydrolysis of the sample. A vortex evaporator is used for CS_2 removal.

3.3 Additional matrix interferences may be caused by contaminants that are coextracted from the sample and from other CS_2 generating compounds. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the sample.

4. SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe

handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[3-5] for the information of the analyst.

4.2 Nabam (ethylenebis(dithiocarbamate)) has been identified as having substantial evidence of carcinogenicity and should be handled according to OSHA regulations.

5. APPARATUS AND MATERIALS

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Sample containers - 40-mL screw cap vials (Pierce No. 13075 or equivalent) each equipped with a polytetrafluoroethylene (PTFE)-faced silicone septum (Pierce No. 12722 or equivalent). Prior to use, wash vials and septa with detergent and rinse with tap and distilled water. Allow the vials and septa to air dry at room temperature, place in a 105°C oven for one hour, then remove and allow to cool in an area known to be free of organics.

5.1.2 Automatic sampler (optional) - Must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated at 4°C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware

5.2.1 Centrifuge tube - 15-mL, conical with Teflon-lined screw cap.

5.2.2 Volumetric flask - 250-mL with glass stopper.

5.2.3 Bottles - 100- to 200-mL capacity with Teflon-lined screw caps.

5.3 Vortex Evaporator - Buchler 3-2200, equipped with sample block to hold 36 15-mL conical bottom centrifuge tubes and appropriate vacuum cover.

5.4 Water bath - Heated, capable of temperature control (±2°C). The bath should be used in a hood.

5.5 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

5.6 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.6.1 Column - 180 cm x 2 mm ID glass, packed with 0.1% SP-1000 on Carbopack C (80/100 mesh) or equivalent. This column was used to develop the method performance statements in Section 14. Alternate columns may be used in accordance with the provisions described in Section 11.1.

5.6.2 Detector - Hall detector operated in the sulfur mode. This detector has proven effective in the analysis of wastewaters for the compounds listed in the scope and was used to develop the method performance statements in Section 14.

6. REAGENTS

6.1 Reagent water - Reagent water is defined as a water in which an interferent is not observed at the MDL of each parameter of interest.

6.2 Hexane - Distilled-in-glass quality or equivalent.

6.3 Sulfuric acid, 12 N - Slowly add 100 mL concentrated sulfuric acid to 200 mL reagent water.

6.4 Sodium phosphate, tribasic, dodeca-hydrate - Baker reagent grade or equivalent.

6.5 Tribasic sodium phosphate, 0.1 M - Dissolve 38 g of tribasic sodium phosphate in reagent water and dilute to 1000 mL with reagent water.

6.6 Stannous chloride - $SnCl_2$ $2H_2O$, ACS grade.

6.7 Stannous chloride reagent - Dissolve 1.5 g stannous chloride in 100 mL 12 N sulfuric acid. Prepare fresh daily.

6.8 Sodium chloride - Heated at 450°C for eight hours.

6.9 Stock standard solutions (0.1 µg/µL) - Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.9.1 Prepare dithiocarbamate spiking solutions by accurately weighing about 0.025 grams of pure material. Dissolve the material in 0.1 M Na_3PO_4 and dilute to volume in a 250-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.9.2 (0.1 µg/µL) Prepare CS_2 stock standard solution by adding 7.9 µL of CS_2 to hexane and diluting to volume in a 100-mL volumetric flask.

6.9.3 Transfer the stock standard solutions into Teflon-sealed screw cap bottles. Store at 4°C. Frequently check standard solutions for signs of degradation or evaporation.

6.9.4 Stock standard solutions must be replaced after six months or sooner if comparison with check standards indicates a problem.

7. CALIBRATION

7.1 Use ziram as the standard for total dithiocarbamates when a mixture of dithiocarbamates is likely to be present. Use the specific dithiocarbamate as a standard when only one pesticide is present and its identity has been established.

7.2 Establish gas chromatographic operating parameters equivalent to those indicated in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.3).

7.3 External standard calibration procedure:

7.3.1 Prepare calibration standards at a minimum of three concentration levels by adding volumes of the CS_2 stock standard to a volumetric flask and diluting to volume with hexane. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the range of concentrations expected in the sample concentrates or should define the working range of the detector.

7.3.2 Using injections of 1 to 5 µL of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for CS_2. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, the average calibration factor can be used in place of a calibration curve.

7.3.3 The working calibration curve or calibration factor must be verified on each working shift by the measurement of one or more calibration standards.

If the response for CS_2 varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared.

7.4 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate the absence of interferences from the reagents.

8. QUALITY CONTROL

8.1 Each laboratory using this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 The laboratory must spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 Select a representative spike concentration for each compound to be measured.

8.2.2 Add a known amount of an individual dithiocarbamate standard to a minimum of four 5-mL aliquots of 0.1 M tribasic sodium phosphate. A representative wastewater may be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.2.3 Calculate the average percent recovery (R), and the standard deviation of the percent recovery (s), for the results. Wastewater background corrections must be made before R and s calculations are performed.

8.2.4 Using the appropriate data from Table 2, determine the recovery and single operator precision expected for the method, and compare these results to the values measured in Section 8.2.3. If the data are not comparable, the analyst must review potential problem areas and repeat the test.

8.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration and parameter being measured.

8.3.1 Calculate upper and lower control limits for method performance as follows:

$$\text{Upper Control Limit (UCL)} = \bar{R} + 3\,s$$
$$\text{Lower Control Limit (LCL)} = \bar{R} - 3\,s$$

where R and S are calculated as in Section 8.2.3. The UCL and LCL can be used to construct control charts[6] that are useful in observing trends in performance.

8.3.2 The laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is

defined as R ± s. The accuracy statement should be developed by the analysis of four aliquots of wastewater as described in Section 8.2.2, followed by the calculation of R and s. Alternately, the analyst may use four wastewater data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly.[6]

8.4 The laboratory is required to collect in duplicate a portion of their samples to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 8.2. If the recovery for a particular compound does not fall within the control limits for method performance, the results reported for that compound in all samples processed as part of the same set must be qualified as described in Section 12.3. The laboratory should monitor the frequency of data so qualified to ensure that it remains at or below 5%.

8.5 Before processing any samples, the analyst should demonstrate though the analysis of a 5-mL aliquot of 0.1 M tribasic sodium phosphate that all glassware and reagents interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a laboratory reagent blank should be processes as a safeguard against laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography

with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

9. SAMPLES COLLECTION, PRESERVATION, AND HANDLING

9.1 Grab samples must be collected in glass containers. Conventional sampling practices[7] should be followed; however, the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of plastic and other potential sources of contamination.

9.2 The samples must be iced or refrigerated at 4° C from the time of collection until extraction.

9.3 Add 15.2 g of tribasic sodium phosphate per 40 mL of sample to the sample to adjust pH to 12-13 at time of collection.

10. SAMPLE CLEANUP AND EXTRACTION

10.1 Place 5 mL of sample in a 15-mL conical centrifuge tube.

10.2 Add 0.75 g of NaCl and shake tube to dissolve salt.

10.3 Add 2 mL of MTBE and process in a vortex evaporator for 10 min with the temperature at 30°C, a vacuum of 30 inches Hg, and the vortex speed control set at 4.5.

10.4 Repeat step 10.3 twice.

10.5 Add 0.75 mL of hexane and 2.5 mL of $SnCl_2$ reagent to the aqueous layer. Cap tube tightly and invert in a water bath at 50° C for 30 min.

10.6 Remove tube from water bath and let cool inverted to room temperatue.

10.7 Shake tube for 1 min without venting. Analyze the hexane layer by GC with a Hall detector in the sulfur mode.

If CS_2 levels are outside of the GC calibration range, the sample can be diluted a known amount with hexane and reanalyzed.

11. GAS CHROMATOGRAPHY

11.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are estimated retention time and MDLs that can be achieved by this method. An example of the chromatography achieved Column 1 is shown in Figure 1. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met. Capillary (open-tubular) columns may also be used if the relative standard deviations of responses for replicate injections are demonstrated to be less than 6% and the requirements of Section 8.2 are met.

11.2 Calibrate the gas chromatographic system daily as described in Section 7.

11.3 Inject 1 to 5 µL of the sample extract using the solvent flush technique[8]. Record the volume injected to the nearest 0.05 µL, and the resulting peak sizes in area or peak height units. An automated system that consistently injects a constant volume of extract may also be used.

11.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.5 If the response for the peak exceeds the working range of the system, dilute the extract with hexane and reanalyze.

11.6 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

12. CALCULATIONS

12.1 Determine the concentration of carbon disulfide in the sample.

12.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor in Section 7.2.2. The concentration of dithiocarbamate in the sample can be calculated as follows:

$$\text{Concentration, } \mu g/L = \frac{(A)(V_t)(M_c)}{(V_i)(V_s)(76)(C)}$$

where:

A = Amount of CS_2 injected, in nanograms
V_i = Volume of extract injected in µL.
V_t = Volume of total extract in µL.
V_s = Volume of water extracted in mL.
M_c = Molecular weight of dithiocarbamate
C = Theoretical number of moles of CS_2 formed per mole of dithiocarbamate.

12.2 Determine the concentration of total dithiocarbamates in the sample as ziram. When a specific dithiocarbamate is being measured, quantitate in terms of the selected pesticide.

12.3 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

12.4 For samples processed as part of a set where the laboratory spiked sample recovery falls outside of the control limits in Section 8.3, data for the affected compounds must be labeled as suspect.

13. METHOD PERFORMANCE

13.1 The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.[9] The MDL concentrations listed in Table 1 were obtained using spiked reagent water samples.[1]

13.2 This method has been tested for linearity of recovery from spiked reagent water and has been demonstrated to be applicable over the concentration range from 10 µg/L to 1000 µg/L.

13.3 In a single laboratory, Battelle Columbus Laboratories, using spiked wastewater samples, the average recoveries of the parameters listed in Section 1.1 presented in Table 2 were obtained. Seven replicates of the wastewater were spiked and analyzed. The standard deviation of the percent recovery is also included in Table 2.[1]

REFERENCES

1. "Determination of Pesticides and Priority Pollutants in Industrial and Municipal Wastewaters," Report for EPA Contract 68-03-1760-Work Assignment 4 (In preparation).

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6. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," EPA-600/4-79-019, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory - Cincinnati, Ohio 45268, March 1979.

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8. Burke, J.A., "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037 (1965).

9. Glaser, J.A. et al, "Trace Analysis for Wastewaters", Environmental Science and Technology, 15, 1426 (1981).

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention Time (Min)(a)	MDL(µg/L)
Amobam	1.3	1.1
Busan 40	1.3	4.4
Busan 45	1.3	1.3
EXD	1.3	5.2
Ferbam	1.3	2.9
KN-Methyl	1.3	2.7
Metham	1.3	3.1
Nabam	1.3	1.6
Nabonate	1.3	0.9
Na DMDTC	1.3	2.8
Thiram	1.3	2.2
Zineb	1.3	4.1
Ziram	1.3	4.6

(a) Retention time of CS_2 under the following conditions: Carbopack C (80/100 mesh) coated with 0.1% SP-1000 packed in a 180 cm long x 2 mm ID glass column with helium carrier gas at a flow rate of 25 mL/min. Column temperature held at 70°C for 3 minutes, programmed at 20°C/min to 120°C, and then held at 120°C for 5 minutes. Column effluent is vented from the Hall detector after elution of CS_2 from the column. Injector temperature and detector temperatures are 200°C. The Hall detector is operated in the sulfur mode following manufacturer's specifications.

TABLE 2. SINGLE LABORATORY ACCURACY AND PRECISION

Parameter	Sample Type(a)	Background µg/L	Spike µg/L	Mean Recovery, %	Standard Deviation	Number of Replicates
Amobam	1	4.6	50	90	7.8	7
	1	4.6	500	93	8.7	7
Busan 40	1	6.6	50	110	7.2	7
	1	6.6	500	100	6.1	7
Busan 85	1	5.9	50	110	5.5	7
	1	5.9	500	100	2.0	7
EXD	1	4.5	50	71	7.5	7
	1	4.5	500	76	2.4	7
Ferbam	1	5.2	50	94	4.8	7
	1	5.2	500	110	1.8	7
KN Methyl	1	5.4	50	90	6.1	7
	1	5.4	500	89	2.5	7
Methan	1	6.2	50	110	5.2	7
	1	6.2	500	84	5.9	7
Nabam	1	4.8	50	62	6.6	7
	1	4.8	500	65	13	7
Nabonate	1	6.1	50	66	11	7
	1	6.1	500	56	12	7
NaDMDTC	1	5.4	50	110	2.5	7
	1	5.4	500	110	4.2	7
Thiram	1	4.5	50	89	2.9	7
	1	4.5	500	82	3.4	7
Zineb	1	5.2	50	87	3.4	7
	1	5.2	500	86	9.4	7
Ziram	1	5.7	50	100	12	7
	1	5.7	500	95	19	7

(a) 1 = Wastewater from a manufacturer of a dithiocarbamate diluted 1000:1 with Columbus POTW secondary effluent.

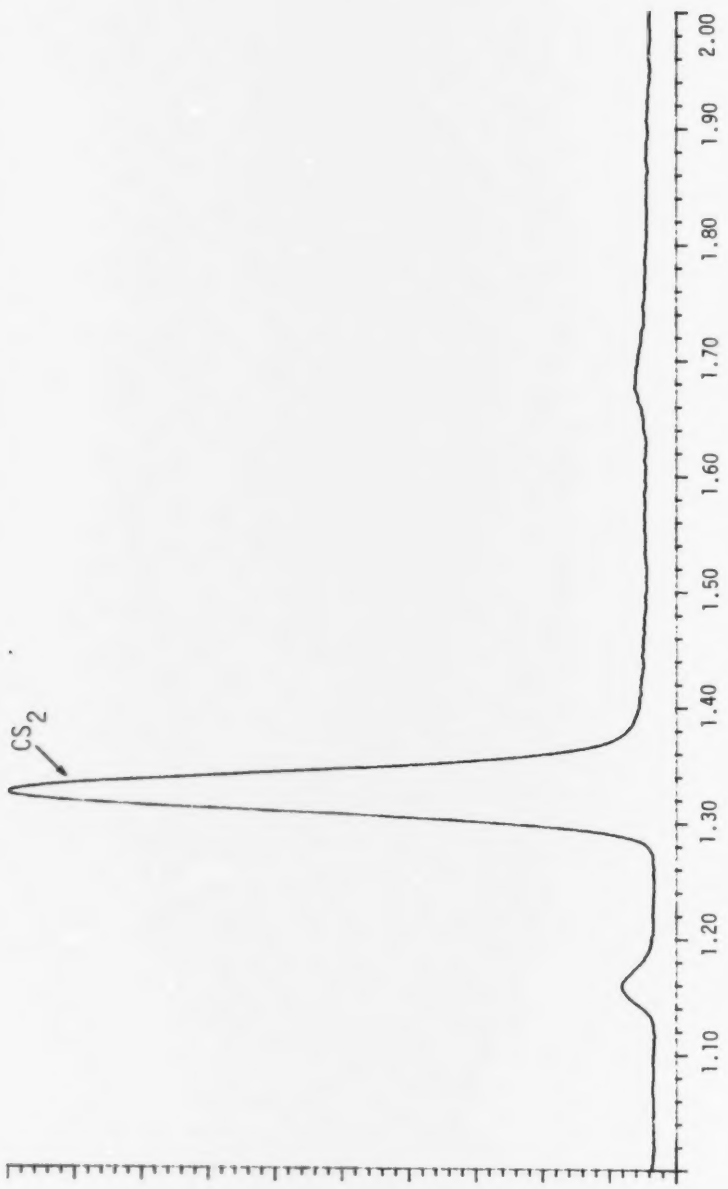

FIGURE 1. GC-HALL CHROMATOGRAM OF 0.1 NG OF CS_2